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Investigation of mechanism involved in TiO_2 and Photo-Fenton photocatalytic degradation of emerging contaminant sucralose in aqueous media

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Abstract

Sucralose is an artificial sweetener persistently present in wastewater treatment and aquatic environments. Two advanced oxidation processes (heterogeneous TiO_2 and homogeneous Fenton photocatalysis) were employed for degradation of sucralose in aqueous phase. The aqueous samples were irradiated under a variety of experiment conditions (pH, light sources) and with different amount of TiO_2, Fe (II) and H_2O_2. The disappearance of the sucralose followed pseudo-first-order kinetic according to the Langmuir-Hinshelwood model, where the rate constant increased with an increase in the initial sucralose concentration. Sucralose and intermediates were easily degraded and within 30 minutes of irradiation complete mineralization was achieved in both advanced oxidation processes. During the oxidation process, the chloride ion was detected and accumulated in solution. Results demonstrated that both heterogeneous TiO_2 and homogeneous photo-Fenton photocatalytic treatments are suitable for the elimination of sucralose from the aqueous solution.

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Keywords: Sucralose, advanced oxidation processed, Photodegradation,TiO_2, Photo-Fenton;

1. Introduction

Sucralose is a new artificial sweetener and is approximately 600 times sweeter than sucrose and widely used in more than 80 countries [1].Sucralose is scarcely absorbed in humans and as much as 92% of the ingested amount is excreted unchanged. It was found in wastewaters with an average concentration of 17.6 ug L^{-1} and screening on

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European rivers. Sucralose has been confirmed in the environment and drinking water sources and recently has been recognized as an emerging environmental contaminant [2]. Sucralose is heat stable and it is likely that sucralose may be widespread in drinking waters in the U.S., persisting through traditional drinking water treatment processes [3-5]. Little is known about the fate and environmental behavior of sucralose. This work aims to comprehend the environmental transformations. Simulated solar irradiation using photo-Fenton and Titania suspension as catalysts are employed to assess the decomposition of sucralose.

2. Experimental

The degradation of Sucralose is conducted in an XPA-7 type photochemical reactor (Xujiang Machine Factory, Nanjing, China) with light intensities at quartz tube positions of 12.7 mW/cm^2 (measured using a UV-A irradiation meter, Beijing Normal University, China), a halogen lamp 100 W and a 100 W xenon lamp are also used as light sources separately. The temperature of the reaction solutions was maintained at 25±1℃ by cooling water circulation. Degradations are performed on 50 mL of aqueous solutions containing the different initial concentrations of sucralose. Aliquots of 2 mL suspension are sampled using a syringe at specific time intervals and filtrated through a 0.45 μm polymer membrane filters in a syringe-end filter. The pH value of the filtrates is determined immediately after filtration.

Sucralose in aqueous solution is measured by HPLC-ELSD. HPLC analysis was performed on a Shimadzu Prominence System. Shim-pack VP-DDS-C18 column (4.6 mm×150 mm, 3 μm) at a flow rate of 0.8 mL min^{-1}. The nebulizer gas was nitrogen of industrial purity grade. The injection volume is 10 μL. The effluent consists of 60% methanol and 40% deionized water (pH =2.5). Sucralose is determined by the retention time of 7.0 min and its concentration is obtained by the peak area.

An ion chromatograph (Dionex ICS-2100). The anions were analyzed using a Dionex AS9HC anion-exchange column quipped with a guard column Dionex Ion Pac, 10 mM $NaHCO_3$ and 4 mM K_2CO_3 as eluent and a flow rate of 0.8 mL min^{-1}. In these experimental conditions, the retention time for chloride ion was 7.20 min. Total organic carbon (TOC) was measured using an analytikjena multi N/C 3100 analyzer which is based on sample oxidation on platinum catalyst at a temperature 800 ℃.

Result and Discussion

Different content TiO_2 treatment: Experiments were carried out before the development of the experimental design, to evaluate the extent of adsorption, hydrolysis and photolysis processes on the transformation. Results obtained, showed, that the experiments occurred in a pure photocatalytic regime, where hydrolysis and direct photolysis processes can be neglected. Moreover, in the considered times, no degradation occurs in the dark (less than 3% of conversion).

The TiO_2 photocatalytic disappearance of Sucralose performed according to the procedure indicated in the experimental section and degradation rate of different content TiO_2 at the same sucralose level under 100 W mercury lamp depicted in Fig. 1. The degradation rate of sucralose was the biggest one when the 0.04g TiO_2 was added. When TiO_2 was added more than 0.04 g, the degradation rate was getting lower. It may because that the more TiO_2 would block the light through the solution in this system.

Photodegradation kinetics of Sucralose: Degradation of chemical compounds have been found to follow pseudo-first-order kinetics. Following these evidences, the equation for pseudo-first order kinetics can be written as

$$R = -\frac{dC}{dt} = k_{obs}C \quad \cdots\cdots\cdots\cdots (1)$$

With the analytic solution as

$$\ln\frac{C_t}{C_0} = -k_{obs}t \quad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

Where C_0 is the initial concentration of sucralose (mg L^{-1}), Ct is the sucralose concentration (mg L^{-1}) measured during the irradiation at time t, and K_{obs} is the pseudo-first-order rate constant (min^{-1}).

Sucralose concentration linear transform versus irradiation time is plotted in Fig.3 at different initial concentrations. In Fig. 2, vertical axis is C_t/C_0 to illustrate overall pseudo-first-order kinetics ($-\ln C_t/C_0=K_{obs}\,t$) in the case of initial concentration less than 100 mg L^{-1}. The pseudo-first-order kinetic model was certified by the linear character of ln (C_0/C_t) versus time. Using linear regression, the degradation data were analyzed using Eq. (2) to determine the overall order and rate constant for the degradation reaction. Accordingly, $\ln C_0/C_t$ was plotted vs t, from which rate constant, K_{obs} was calculated as the slope. This assumption was true and right. The pseudo-first-order rate constant of the degradation after 30 min of reaction time was calculated from linear regression ln(C0/Ct) versus time plots with all regression coefficients greater than 0.98.

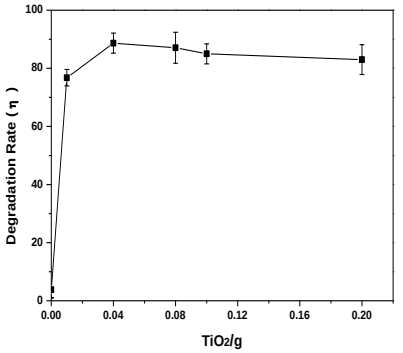

Fig. 1. Degradation rate of different content TiO_2 treatment

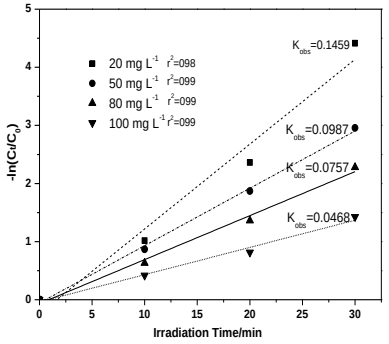

Fig. 2 Linear transform -ln C/C_0 vs. time for Sucralose

The pseudo-first-order rate constant k_{obs} is obtained from the slop of the concentration versus irradiation time curve. The initial rate ($R_0=-k_{obs}C_0$) thus can be obtained. The experiments are carried with a range of initial concentrations from 20, 50, 80 and 100 mg L^{-1}. The results are shown in Fig. 2. It could be seen that the initial rate of sucralose photodegradation increases with increasing sucralose concentration. The observe rate constant k_{obs} of sucralose decreases from 0.1459 min^{-1} to 0.0468 min^{-1} with increasing sucralose concentration from 20 mg L^{-1} to 100 mg L^{-1}.

In Fig. 3, the degradation rate constants obtained were 0.2715 min^{-1},0.1414 min^{-1}, and 0.0861min^{-1}, respectively, for the different initial concentrations of sucralose which were 50, 100 and 150 mg L^{-1}. The rate constants all decreased with increased initial concentration. The results showed that these reactions accorded with a pseudo-first-order, and the reactive rate was decreased with increasing concentration in the sucralose linearity range (50-150 mg L^{-1}).

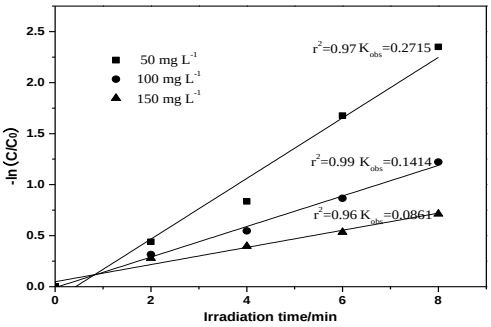

Fig. 3. Linear transform for sucralose in the photo-Fenton system

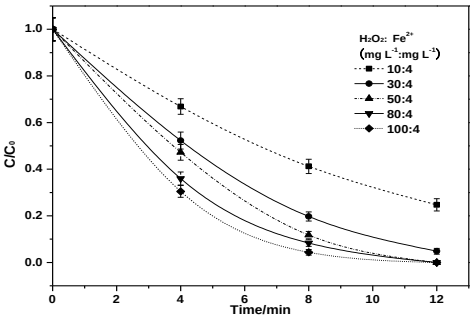

Fig. 4 C/C_0 VS irradiation time under the different $[H_2O_2]/[Fe^{2+}]$

Degradation of different concentration of Sucralose in photo-Fenton was shown on Fig.3. From the Fig. 3, degradation of sucralose in photo-Fenton system was also observed to follow pseudo-first-order kinetics and the reactive rate was decreased with increasing concentration.

Fig.4 shows the effect of $[H_2O_2]/[Fe^{2+}]$ on sucralose degradation. Sucralose was almost degraded in 12 minutes especially in high ratio of $[H_2O_2]/[Fe^{2+}]$. Compared with TiO_2 system within 30 minutes, it was faster in Photo-Fenton system. Degradation efficiency is increased with increasing amounts of Fe (II) and H_2O_2.With respect to Fe (II) concentration in Photo-Fenton system, increasing iron concentrations favored the treatment of sucralose especially at moderate amounts of H_2O_2. Lower iron (II) will consume less H_2O_2 in the initial reaction period.

Different ratio of $[H_2O_2]/ [Fe^{2+}]$ have great effect on the Sucralose degradation. When ratio of $[H_2O_2]/ [Fe^{2+}]$ was 10:4, 25% sucralose did not be degraded in 12 minutes. The reactive rate was increased with ratio of $[H_2O_2]/ [Fe^{2+}]$ by studying the kinetics. For ratio of 50:4, 80:4 and 100:4, sucralose have been almost degraded in 12 minutes. Consideration of economic reason, in this photo-Fenton system, the optimal ratio of $[H_2O_2]/ [Fe^{2+}]$ was 50:4.

Mineralization: Total organic carbon measurements were carried out on samples subjected to heterogeneous photocatalysis, to assess sucralose mineralization. As arises from the temporal profiles shown in Fig.5, sucralose and its intermediates were completely degraded, comparing the disappearance profile of sucralose with the total organic carbon curve (TOC), we noted that mineralization occurs fast. Total organic carbon was halved after about 15 min of irradiation in TiO_2 system and After 30 minutes of irradiation, complete mineralization is achieved in TiO_2 system.

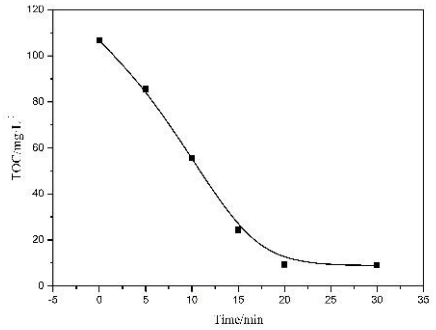

Fig. 5. Curve of TOC in system of TiO_2 photocatalysis

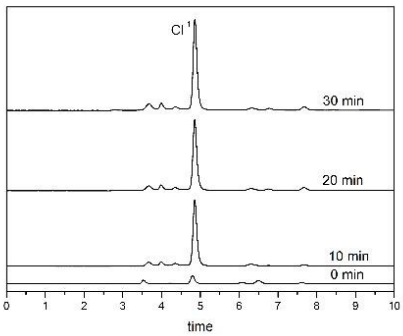

Fig. 6. Chromatography of chloride ion in the solution

Chloride ion release: Sucralose breakage occurs with both treatment processes and was catalytically dechlorinated in two system(Fig.6). Sucralose contains three chlorine atoms, two of which are present in $-CH_2Cl$ groups. Given that many chlorinated compounds are known to be toxic to humans, including chloromethane (CH_3Cl), the incomplete degradation of sucralose could yield undesired byproducts. Thus, it is important to know whether it will release chloride ion or not. The chloride ion in the solution during the different time of the process was shown in Fig. 6. The concentration of chloride ion increase with time. During the oxide process, the chloride ion sustained release. It seems that the photocatalytic degradation lead to almost complete DE chlorination after 30 minutes irradiation.

The result observed by ion chromatograph analysis indicted that full dechlorination of sucralose during advanced oxidation is possible. The dechlorination begins with the chlorine on the cyclic moiety, which is the weakest C-Cl bond of the molecule, and continues with the chlorines on the methyl groups with increasing treatment. The hydroxyl group is the most likely substitute for the chlorine group in advanced oxidation.

4. Conclusion

In this study, it clearly points out that both heterogeneous TiO_2 and homogeneous Photo-Fenton photocatalytic treatments are suitable for the elimination of sucralose from the aqueous solution. When initial sucralose concentration is increased, the degradation rate constant was lower, resulting in longer half-life. The photodegradation of sucralose follows pseudo-first-order kinetics under the different light sources.

Sucralose was easily degraded under both photocatalytic and photo-Fenton treatments. The conversion of sucralose depends on the operating conditions employed. Sucralose and intermediates were degraded and completely mineralized. During the oxide process, the chloride ion sustained release.

Acknowledgements

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References

1. Schleifer D. Sweet Stuff: An American History of Sweeteners from Sugar to Sucralose. *Technol Cult* 2013, 54: 205-207.
2. Soh L, Connors KA, Brooks BW, Zimmerman J. Fate of Sucralose through Environmental and Water Treatment Processes and Impact on Plant Indicator Species. *Environ Sci Technol* 2011, 45: 1363-1369.
3. Oppenheimer J, Eaton A, Badruzzaman M, Haghani AW. Occurrence and suitability of sucralose as an indicator compound of wastewater loading to surface waters in urbanized regions. Water Res 2011, 45: 4019-4027.
4. Richardson S D.Environmental Mass Spectrometry: Emerging Contaminants and Current Issues. *Anal Chem* 2012, 84: 747-778.
5. Tollefsen K E, Nizzetto L, Huggett D B. Presence, fate and effects of the intense sweetener sucralose in the aquatic environment. *Sci Total Environ* 2012, 438: 510-516.